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ELECTRODEPOSITION OF CATALYTICALLY ACTIVE Ni-Mo ALLOYS

ELEKTROOSADZANIE AKTYWNYCH KATALITYCZNIE STOPÓW Ni-Mo

The work presents results of researches over the deposition of Ni-Mo alloys through the electrolysis conducted in galvanostatic conditions. In order to improve adhesion and aesthetic properties of the deposited alloys, SLS was added to the bath as a surface active agent. The influence of electrolyte pH was tested as well as concentrations of particular components on the composition, structure, cathodic current efficiency of the electrolysis process and catalytic activity of alloys in the process of hydrogen evolution. A positive influence of addition of molybdenum on catalytic activity was observed occurring in lowering the Tafel's slope within the activation control range from 122 mV/dec (Ni) to 21 mV/dec (Ni-28.5Mo) for a reaction of water molecules reduction in 8 M NaOH at 90°C.

Keywords: Ni-Mo alloys, electrodeposition, hydrogen evolution reaction

W pracy zaprezentowano wyniki badań nad otrzymywaniem stopów Ni-Mo na drodze elektrolizy prowadzonej w warunkach galwanostatycznych. Celem poprawy przyczepności oraz walorów estetycznych otrzymywanych stopów do kąpieli dodano SLS w roli środka powierzchniowo czynnego. Przebadano wpływ pH elektrolitu oraz stężenia poszczególnych składników na skład, strukturę, katodową wydajność prądową procesu elektrolizy oraz właściwości katalityczne stopów w procesie wydzielania wodoru. Zaobserwowano pozytywny wpływ dodatku molibdenu na aktywność katalityczną przejawiający się w spadku nachylenia Tafela w zakresie kontroli aktywacyjnej z 122mV/dec (Ni) do 21 mV/dec (Ni-28.5Mo) dla reakcji redukcji cząsteczek wody w 8 M NaOH w 90°C.

1. Introduction

Some elements such as P, Ge, W and Mo cannot be obtained through electrolysis of water solutions. Whereas, it is possible to deposit the elements with other elements from ferrous metals group. The phenomenon was explained and named as induced co-deposition for the first time by Brenner [1]. Żabiński et al. applying induced co-deposition obtained alloys of Co with Mo [2] and P [3] characterised by good adhesion to the surface of the electrode and a low value of the Tafel's slope for hydrogen evolution reaction (HER). As it is known, Ni-Mo alloys feature high resistance to corrosion [4] and catalytic activity in the process of hydrogen evolution through water solutions electrolysis [5], therefore the authors made an attempt to deposit them through electrolysis of sulphate solutions. The alloys are mainly deposited from citrate and tartrate solutions [6, 7]. The process mechanism is complicated. Zeng et al. tested the process of co-deposition Ni with Mo from citrate solutions and they suggested a mechanism in which molybdate anion (MoO_4^{2-}) is reduced to MoO_4 which is subsequently reduced to a metallic form by hydrogen accumulated on the surface of Ni inducing co-deposition [8].

The work presents a discussion over electrolysis parameters influence on the composition, structure and catalytic properties of Ni-Mo alloys.

2. Experimental details

The electrolyte was prepared by dissolution of $Na_2MoO_4 \cdot 2H_2O$, $NiSO_4$, $Na_3C_6H_5O_7 \cdot 5H_2O$, SLS and saccharine in deionized water. Solution pH was adjusted by the addition of NaOH. The tests were performed at pH of 6, 8 and 10. The compositions of baths used in tests were placed in Tab. 1.

Alloys were deposited onto Cu substrate of 2.3 cm² area. The counter electrode (CE) was platinum sheet (Pt). The Cu substrate was etched before the use in temperature of 60°C ($HNO_3:CH_3COOH:H_3PO_4 - 1:1:1$). Temperature of electrolyte for deposition was 20°C. Alloys were deposited at galvanostatic conditions at current density values of 5, 10 and 20 mA/cm². Elemental quantitative analysis was conducted with the use of WDXRF technique. Phase analysis was performed by XRD method. The catalytic activity of deposits was tested

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in 8 M NaOH at 90°C. The Ag/AgCl (3 M KCl) electrode was used as the reference electrode.

TABLE 1

Baths composition

	Bath		
	◆	▲	●
	Concentration, M		
Na ₂ MoO ₄ · 2H ₂ O	0.035	0.05	0.05
NiSO ₄	0.75	0.5	0.75
Na ₃ C ₆ H ₅ O ₇ · 5H ₂ O	0.45	0.45	0.45

3. Experimental results

The alloys were deposited through electrolysis conducted in galvanostatic conditions from electrolytes of compositions given in Tab. 1. The deposition process was conducted for 120 min applying anodic current density of 20 mA/cm². In case of electrolysis conducted in solutions of pH 8 and 10 no cathodic deposits were observed on the surface of the working electrode. Alloys featuring the best adhesion to the surface and gloss were deposited from electrolyte of pH 6 and composition ▲. In order to improve deposits adhesion properties to the surface and their aesthetic properties, SLS was added to the electrolyte and the value of cathodic current density was lowered to 10 mA/cm² and at that value tests of the influence of Na₂MoO₄ · 2H₂O concentration on the composition of obtained Ni-Mo alloys and cathodic current efficiency of the electrolysis process were performed (Fig. 1).

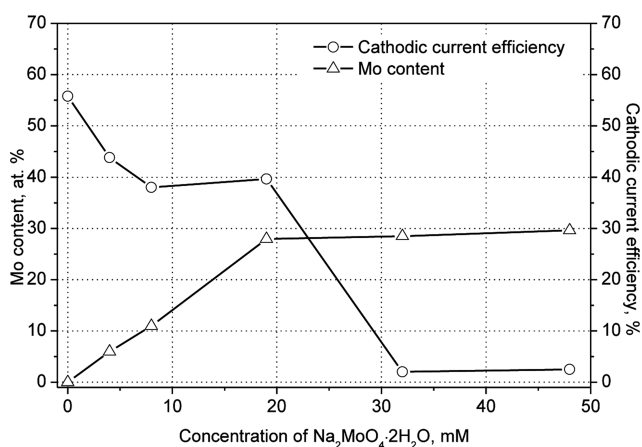


Fig. 1. The influence of Na₂MoO₄·2H₂O on cathodic current efficiency and composition of deposited alloys

The analysis of elemental composition allowed a statement that it is possible to co-deposit Ni with Mo from the applied electrolytes. The highest content of Mo ca 30 at % was featured by alloys deposited from electrolyte of 48 mM Na₂MoO₄ · 2H₂O concentration. Molybdenum salt concentration higher than 19 mM no longer causes a significant increase of molybdenum content in cathodic deposits. However, a negative influence of sodium molybdate addition on cathodic current efficiency was observed causing its decrease from 56%

for electrolyte without molybdate addition to 2.5% for electrolyte with 48 mM Na₂MoO₄ · 2H₂O. The significant decrease in current efficiency of alloys deposited from electrolytes of sodium molybdate concentration higher than 19 mM can be connected with the mechanism of alloys crystallization. Alloys deposited from electrolytes of mM Na₂MoO₄ · 2H₂O concentration up to 19 mM feature a FCC structure. Further increase of molybdate concentration results in formation of amorphous structure (Fig. 2). A decrease of current efficiency is directly caused by a parallel run process of hydrogen ions reduction. The change of cathodic deposits structure is also connected with the change of overvoltage value for a reaction of water molecules reduction. The obtained results indicate that overvoltage is lower for alloys of amorphous structure. The recorded diffractogram (Fig. 2) shows, apart from peaks indicating presence of cathodic deposits, three peaks corresponding to Cu substrate, at values of 2θ = 43.5°, 50.41° and 74.16°, respectively.

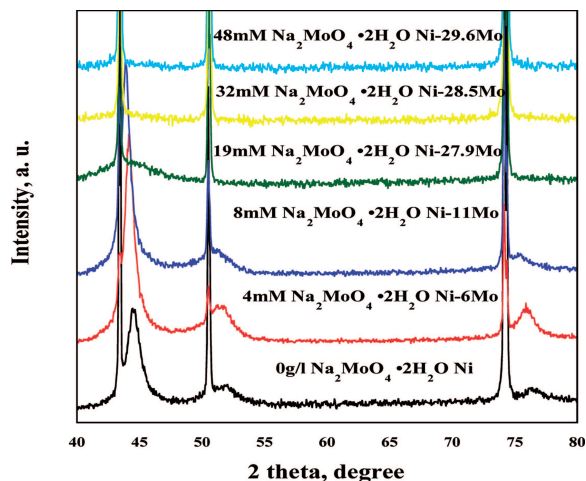


Fig. 2. XRD diffraction patterns for alloys deposited from electrolytes of different concentration of sodium molybdate

Electrocatalytic properties of the obtained alloys were also tested. Overpotential of hydrogen evolution on the obtained alloys was determined based on the dependence (1).

$$\eta = E_i - E_s \quad (1)$$

where: E_i – potential of electrode polarised by electric current flow (defined in galvanostatic measurements ($t = 120$ s) with the use of potentiostat/galvanostat Autolab PGSTAT30 in 8 M NaOH at 90°C), E_s – stationary potential (registered for electrode not polarised after $t = 240$ s). The Tafel's line within activation control range is described by the equation (2).

$$\eta = a + b \cdot \log(i) \quad (2)$$

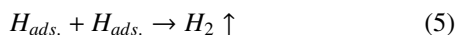
where:

$$b = \frac{dE}{d \log(i)} = 2.303 \cdot \frac{R \cdot T}{\alpha \cdot F} \quad (3)$$

R – gas constant (8.314 J · mol⁻¹ · K⁻¹), T – temperature (K), α – transfer coefficient, F – Faraday's constant (96 485 C · mol⁻¹).

In alkaline environment the complete process of hydrogen evolution is described by two reactions:





Theoretical values of the Tafel's slope for an electrode process controlled respectively by reactions (4) or (5) at temperature of 363 K, assuming that symmetry coefficient $\beta = 0.5$ are to be found in Tab. 2.

TABLE 2
Theoretical Tafel's slopes at 363 K (k_1 – number of electrons in the rds process, k_2 – number of electrons replaced before the rds process, ν – stoichiometric coefficient, RDS – rate determining step)

RDS	k_1	k_2	ν	$\alpha = k_1 \cdot \beta + \frac{k_2}{\nu}$	b
(4)	1	0	2	0.5	144 mV/dec
(5)	0	2	1	2	36 mV/dec

Therefore, testing Tafel's line slope, RDS can be concluded. If the Tafel's slope is ca 144 mV/dec, the slowest phase of the hydrogen evolution process is the water molecules reduction. For slope of ca 36 mV/dec it is a recombination of hydrogen atoms adsorbed on the metal surface.

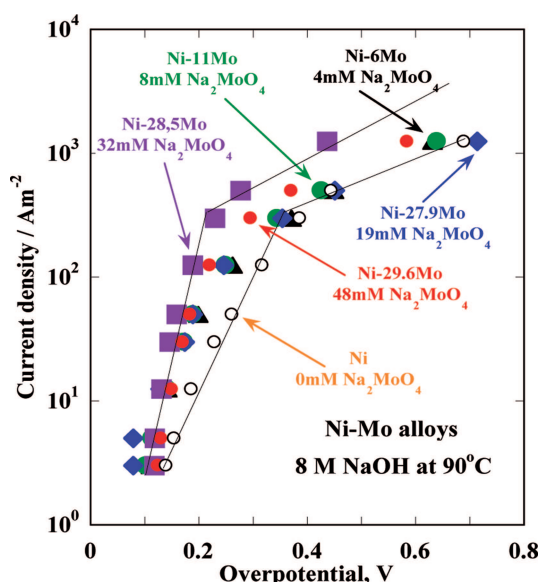


Fig. 3. $\eta - \log(i)$ – dependences for deposited alloys

Fig. 3 presents tests results of catalytic activity measurements of the obtained Ni-Mo alloys for the reaction of water molecule reduction. The lowest Tafel's slope is featured by Ni-28.5Mo alloy and amounts at 21 mV/dec which indicates that the slowest step in the process of hydrogen evolution on it through water molecules reduction is recombination of hydrogen atoms adsorbed on the alloy surface. Addition of Mo to Ni caused a significant improvement of electrocatalytic properties.

4. Conclusions

The conducted tests indicate a possibility to deposit through electrolysis conducted in galvanostatic conditions Ni-Mo alloys of catalytic properties for HER in alkaline environment. The best catalytic activity was presented by the alloy deposited from electrolyte of 32 mM $Na_2MoO_4 \cdot 2H_2O$ concentration and at pH 6. Cathodic current efficiency of the electrolysis in this case amounted at ca 40%. The alloy contained 28.5 at. % Mo, and the Tafel's slope for the process of hydrogen evolution on it amounted at 21 mV/dec. The conducted tests indicate a positive influence of molybdenum addition on electrocatalytic properties for HER.

Acknowledgements

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REFERENCES

- [1] A. Brenner, Electrodeposition of Alloys, Academic Press, New York (1963).
- [2] P.R. Żabiński, K. Mech, R. Kowalik, Co-Mo and Co-Mo-C alloys deposited in a magnetic field of high intensity and their electrocatalytic properties, Archives of Metallurgy and Materials **57**, 127 (2012).
- [3] P. Żabiński, M. Górski, R. Kowalik, Influence of Superimposed External Magnetic Field onto Electrodeposition of Co-P Alloys for Hydrogen Evolution, Archives of Metallurgy and Materials **54**, 1157 (2009).
- [4] P. Prioteasa, F. Golgovici, G. Sbircea, L. Anica, T. Visan, Electrodeposition, Structure and Corrosion Behaviour of Ni-Mo Alloys from Citrate Aqueous Electrolyte, Rev. Chim-Bucharest **61**, 1046 (2010).
- [5] Q. Han, S.A. Cui, N.W. Pu, J.S. Chen, K.R. Liu, X.J. Wei, A study on pulse plating amorphous Ni-Mo alloy coating used as HER cathode in alkaline medium, Int. J. Hydrogen Energ. **35**, 5194 (2010).
- [6] R.K. Shervedani, A. Lasia, Study of the hydrogen evolution reaction on Ni-Mo-P electrodes in alkaline solutions, J. Electrochem. Soc. **145**, 2219, (1998).
- [7] Y. Zeng, S.W. Yao, X.Q. Cao, H.X. Huang, Z.Y. Zhong, H.T. Guo, Electrodeposition mechanism of Ni-Mo-P alloy in the solution of ammoniac citrate, Chinese J. Chem. **15**, 193 (1997).
- [8] Y. Zeng, M. Ma, X.M. Xiao, Z.L. Li, S.X. Lian, S.M. Zhou, Kinetic model of induced codeposition of Ni-Mo alloys, Chinese J. Chem. **18**, 29 (2000).